
V.P.5 Surface-Directed Fabrication of Integrated Membrane-Electrode Interfaces

G. Kane Jennings (Principal Investigator)

Vanderbilt University
Box 1604, Station B
Nashville, TN 37235
Phone: (615) 322-2707; Fax: (615) 343-7951
E-mail: kane.g.jennings@vanderbilt.edu

DOE Program Office: BES, Materials Sciences
and Engineering Division

DOE Program Manager: Dr. Bonnie Gersten
E-mail: Bonnie.Gersten@science.doe.gov

Objectives

Current fabrication approaches^{1,2} for proton exchange membrane (PEM) fuel cells rely on ill-defined, planar interfaces that reduce the performance of the system. The departure from planarity to 3-D interfaces with porosity should provide a boost in power³ due to additional surface area for catalysis to support higher mass transfer rates.⁴ In this project, we are investigating the integration of electrode/catalyst support, gas diffusion pathways, and ionomer into a single network based on a bottom-up, surface-directed approach. Our efforts are focusing on (1) the preparation of surface-initiated ionomer that can be grown from electrodes of essentially any geometry and is chemisorbed to the active electrode surface, and (2) the integration of this ionomer with both planar and porous electrodes that are atomically modified by Pt catalysts.

Technical Barriers

The departure from planarity to porous systems creates difficulties in integrating ionomer and catalyst uniformly throughout the porous electrode structure. We are developing an approach where the electrode surface directs the deposition of catalyst and the growth of ionomer, monomer by monomer, to achieve an exceptional level of control over the composition and structure at this vital interface. Focusing initially on the cathode, our system consists of a thin nanoporous gold support that is atomically modified by a Pt monolayer for ultra-low catalyst loadings and is integrated with ionomer through surface-initiated approaches. The molecularly designed ionomer contains a fluorocarbon matrix for good O₂ transfer with sulfonate-lined channels to promote proton transfer.

Abstract

By integrating catalyst, ionomer, and gas diffusion layer into a porous electrode architecture, the proposed research renewal seeks to molecularly transform the cathodic interface of a proton exchange membrane fuel cell. The proposed 3-D cathode consists of a thin porous gold support that is atomically modified by a Pt monolayer for ultra-low catalyst loadings and is integrated with ionomer through surface-initiated polymerization (SIP). The surface-directed deposition of catalyst and ionomer enables high control over the composition within nanoporous electrodes. Results under the current funding have demonstrated that proton-conducting polymers can be grown from various surfaces by surface-initiated ring-opening metathesis polymerization (SI-ROMP) of 5-(perfluoro-n-alkyl) norbornenes and subsequent rapid sulfonation of the internal olefins. These films can be integrated with Pt catalysts at interfaces for high performance in the oxygen reduction reaction.

While much of our initial work has focused on materials synthesis and integration, our most recent work is utilizing these systems to gain fundamental insight on the effects of materials composition and properties at 3-D interfaces to optimize cathode performance. Specifically, we seek to (1) establish greater versatility in the preparation of nanoporous electrodes to control pore size, porosity, and electrode thickness; (2) develop new “interfacial” ionomer systems from surface initiation, grafting, and self-assembly to fundamentally assess the effects of interfacial bonding, ionomer composition and structure, as well as free volume within the pores, on the performance of the electrode; and (3) extend these strategies to commercial carbon supports. The successful completion of these objectives will yield well-defined and molecularly integrated materials systems to achieve high utilization of catalyst/electrode surface area with ultra-low catalyst loadings. This research will improve the basic understanding of the complex reaction and transport processes that occur near the triple interface in a fuel cell environment.

Progress Report

Our initial efforts reported the surface-initiated ROMP of n-alkylnorbornenes to control film thickness and composition at electrode surfaces⁵ and the sulfonation of these films to facilitate proton transfer.⁶ More recently, we have developed an approach for the SI-ROMP of partially fluorinated films from

5-(perfluoro-*n*-alkyl)norbornenes,⁷ their integration with Pt catalysts at an electrode surface,⁸ and their polymerization from porous supports, including carbon paper⁹ and nanoporous gold leaf electrodes,¹⁰ as described below.

I. Growth of Partially Fluorinated Ionomer Films.

A major emphasis of this project has been to prepare partially fluorinated ionomer films through a surface-initiated polymerization (SIP). SIPs provide the ability to grow films of controlled thicknesses from substrates of nearly any geometry, such as 3-D, porous catalyst/diffusion layers. However, SIP of fluorinated monomers has been historically difficult due to the steric hindrance of the fluorocarbon functionality. In an important innovation, we have developed the surface-initiated ring-opening metathesis polymerization (SI-ROMP) of (perfluoro-*n*-alkyl)norbornenes (NBFn) to form partially fluorinated polymer films (pNBFn) of tunable thicknesses ranging from tens of nanometers to microns on various substrates.⁷ The polymers are tethered to the surface on one end and upon sulfonation, have the general repeat structure as shown in Figure 1. By varying the fluorocarbon side chain of the monomer, we can tune the structure (SEM and infrared spectroscopy), transport properties (electrochemical impedance spectroscopy), and critical surface energies (contact angles) of the films.⁷ Our results indicate that the fluorocarbon side chains self-organize into fluorocarbon-rich regions. Structuring of the polymer in this manner should be highly effective for PEM fuel cell applications since O₂ would transfer through the fluorocarbon regions and protons would transfer through the sulfonated regions. We have recently published methods to sulfonate hydrocarbon⁶ and fluorocarbon⁸ films prepared by this method.

II. Extension of SI-ROMP to Carbon Paper.

To demonstrate that pNBFn films can be grown from various substrates, including those with technological relevance, we have developed an approach to grow these films from graphitic carbon paper,⁹ which has 3-D fibrous structure. Since graphitic fibers are relatively inert, we expose the carbon paper to an oxygen plasma for up to 1 min to create a few dispersed oxygen-containing surface sites across the fiber surface before attaching the polymerization initiator, which enables SI-ROMP from the fiber surface, as shown in SEM images of Figure 2. These pNBFn-modified carbon paper electrodes exhibit superhydrophobic surface properties, meaning that an impinging stream of water bounces off the surface and that a water drop on the surface will exhibit a contact angle of > 150°. Conformal, hydrophobic coatings such as these can greatly aid water management at PEM cathodes.¹¹ These films can also

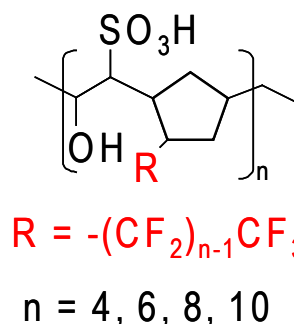


FIGURE 1. Schematic of pNBFn repeat structure. These polymers are grown from surfaces via surface-initiated ROMP.

be sulfonated to provide surface-attached ionomer to the graphitic carbon surface.

III. Integration of Ionomer Films at Pt-Modified Electrodes.

The direct wiring of ionomer films to electrode surfaces is beneficial to reduce interfacial resistances and boost electrochemical performance in many energy-related applications. However, a key issue regarding the direct chemical wiring of ionomer to electrode/catalyst interfaces is the possible deactivation of the catalyst by the chemisorption event. We⁸ have reported the surface-initiated growth and sulfonation of polynorbornene (pNB), poly(*n*-butylnorbornene) (pNBH4), and poly(perfluoro-*n*-butyl)norbornene (pNBF4) to prepare ionomer films on gold electrodes that are pre-modified by an atomic layer of Pt. Our goal here was to demonstrate proof-of-concept systems for the integration of chemisorbed ionomer and catalyst at model electrode surfaces. In this manuscript, we have made some important conclusions. First, the ionomer films can be grown from Pt-monolayer-modified surfaces without compromising the performance or integrity of the Pt. Second, sulfonated films derived from NBF4 and NBH4 yield more anodic potentials for oxygen reduction than those derived from NB or unfunctionalized electrodes. These improvements are consistent with hydrophobic structuring by the fluorocarbon or hydrocarbon side groups to generate pathways for enhanced O₂ permeation near the interface. Third, we demonstrate a method to electrochemically “clean” ionomer/electrode interfaces. For example, in surface-initiated polymerizations, only a small fraction (often < 10%) of the surface sites typically yield polymer. For electrochemical applications, these inactive adsorbates can block catalyst sites on the surface and hamper the performance of the electrode. Here, we demonstrate the ability to electrochemically reduce and desorb these short, non-polymeric adsorbates from the surface without affecting the surface-attached ionomer.

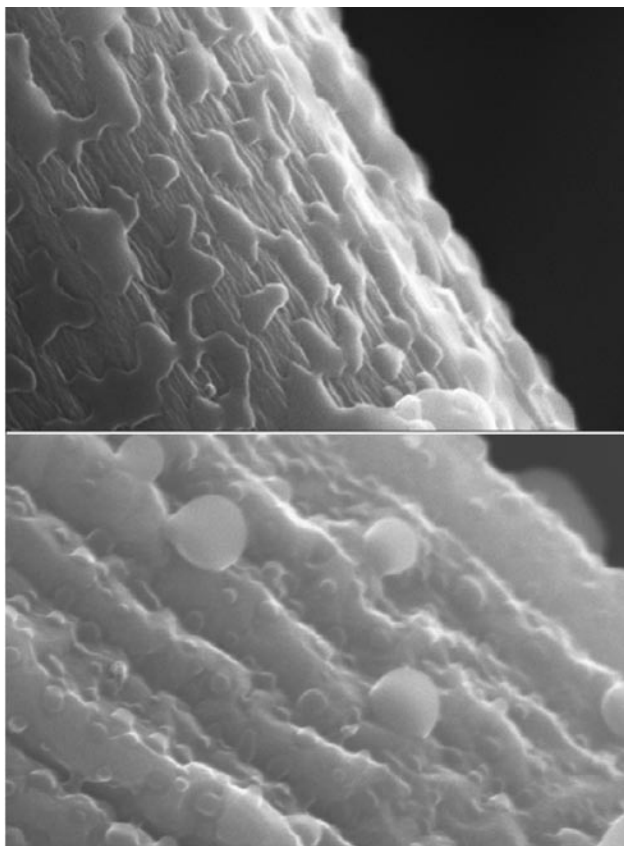


FIGURE 2. SEM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of pNBF6 grown from graphitic carbon fibers after initial exposure to O_2 plasma for 30 s (top) or 60 s (bottom).

We show that desorption of these short molecular components from the polymer/electrode interface reduces interfacial impedance and greatly improves the performance of the Pt /Au electrode toward oxygen reduction.

IV. Growing Ionomer Within Nanoporous Electrodes.

A key element of this project is to grow ionomer films within nanoporous electrodes to ultimately integrate ionomer, catalysts, and pores for gas diffusion into a single network. We have developed a simple fabrication scheme to prepare nanoporous electrodes¹² with several adaptations to the technique developed by Ding et al.¹³ that makes use of a graphite roller. Successful SI-ROMP of pNBF6 throughout the nanoporous electrode has been achieved by controlling the monomer concentration in relation to the average pore size as evidenced by a combination of SEM (Figure 3), infrared spectroscopy, and electrochemical impedance spectroscopy.

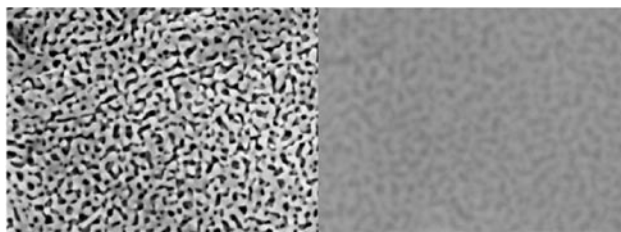


FIGURE 3. SEM images ($0.8\ \mu\text{m} \times 1\ \mu\text{m}$) of nanoporous gold electrodes with a partial (left) and complete (right) coating of pNBF6.

Future Directions

For the next period, we will build on our successes with surface-initiated, partially fluorinated ionomers and nanoporous electrode films to investigate the following issues:

- Examine the effect of fluorocarbon side chain length and sulfonation levels on the transport of O_2 and protons through the membranes.
- Synthesize short pNBF_n oligomers that are terminated in thiol functionality for directed self-assembly at both planar and nanoporous Pt/Au interfaces. Sulfonate these oligomers after assembly and investigate their effectiveness in promoting oxygen reduction.
- Combine the most successful approaches from the preceding two objectives with carbon paper electrodes and back-fed O_2 to investigate cathode performance under realistic operating conditions.

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